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(54) **NAPHTHENIC ACID CORROSION INHIBITION USING NEW SYNERGETIC COMBINATION OF PHOSPHORUS COMPOUNDS**

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(58) **Field of Classification Search**
None
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

1,872,091	A	8/1932	Mougey	
2,316,078	A	4/1943	Loane at al.	
2,316,087	A	4/1943	Gaynor et al.	
2,688,612	A *	9/1954	Watson	562/9
2,915,517	A	12/1959	Le Suer	
3,132,975	A	5/1964	Freud	
3,145,886	A	8/1964	Goodwin	
3,201,438	A	8/1965	Reed	
3,281,359	A	10/1966	Oberender et al.	
3,324,032	A	6/1967	O'Halloran	
3,428,561	A	2/1969	Lesuer	
3,459,662	A *	8/1969	Hu	508/349
3,460,898	A	8/1969	Rusch	
3,489,682	A	1/1970	Lesuer	
3,531,394	A	9/1970	Koszman	
3,668,237	A	6/1972	Cyba	
3,909,447	A	9/1975	Redmore et al.	
4,024,049	A	5/1977	Shell et al.	
4,024,050	A	5/1977	Shell et al.	
4,105,540	A	8/1978	Weinland	
4,443,609	A	4/1984	Oude Alink et al.	
4,542,253	A	9/1985	Kaplan et al.	
4,578,178	A	3/1986	Forester	
4,600,518	A	7/1986	Ries et al.	
4,842,716	A	6/1989	Kaplan et al.	
4,906,391	A *	3/1990	Andress	508/324
4,927,561	A	5/1990	Forester	
4,941,994	A	7/1990	Zetlmeisl et al.	
5,182,013	A	1/1993	Petersen et al.	
5,252,254	A	10/1993	Babaian-Kibala	
5,314,643	A *	5/1994	Edmondson et al.	208/47
5,484,542	A	1/1996	Cahoon et al.	
5,500,107	A *	3/1996	Edmondson	208/47
5,552,085	A	9/1996	Babaian-Kibala	
5,611,991	A	3/1997	Naraghi	
5,630,964	A	5/1997	Babaian-Kibala et al.	

(Continued)

FOREIGN PATENT DOCUMENTS

EP	0 565285	B1	5/1997
EP	1063276	A1	12/2000

(Continued)

OTHER PUBLICATIONS

International Search Report dated Mar. 23, 2009.

(Continued)

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(57) **ABSTRACT**

The present invention relates to the field of processing hydrocarbons which causes corrosion in the metal surfaces of processing units. The invention addresses the technical problem of high temperature naphthenic acid corrosion and sulphur corrosion and provides a solution to inhibit these types of corrosion. The three combination compositions are formed by three mixtures separately, with one mixture obtained by mixing compound A, which is obtained by reacting high reactive polyisobutylene (HRPIB) with phosphorous pentasulphide in presence of catalytic amount of sulphur with compound B such as trialkyl phosphate and second mixture obtained by mixing compound A with compound C such as phosphite like di-isodecyl phenyl phosphite, and third mixture obtained by mixing compound A with compound D such as a phosphonate, wherein each of these three mixtures independently provide high corrosion inhibition efficiency in case of high temperature naphthenic acid corrosion inhibition and sulphur corrosion inhibition. The invention is useful in all hydrocarbon processing units, such as, refineries, distillation columns and other petrochemical industries.

48 Claims, No Drawings

(56) References Cited

U.S. PATENT DOCUMENTS

5,725,611	A	3/1998	Wright et al.	
5,863,415	A	1/1999	Zetlmeisl	
6,512,133	B1	1/2003	Götzmann et al.	
7,122,508	B2	10/2006	Boffa	
2002/0107150	A1	8/2002	Mikami et al.	
2003/0201207	A1 *	10/2003	Eaton et al.	208/265
2005/0044778	A1	3/2005	Orr	
2005/0234184	A1	10/2005	Doring et al.	
2007/0119747	A1	5/2007	Harrell et al.	
2010/0126842	A1	5/2010	Subramaniyam	
2010/0264064	A1	10/2010	Mahesh	
2011/0160405	A1	6/2011	Subramaniyam	
2011/0214980	A1	9/2011	Subramaniyam	

FOREIGN PATENT DOCUMENTS

GB	8667		0/1907
GB	792553		3/1958
WO	2006049980	A2	5/2006
WO	2008005058	A1	1/2008
WO	2008120236	A2	10/2008
WO	2008120236	A3	10/2008
WO	2008122989	A2	10/2008
WO	2008122989	A3	10/2008
WO	2008122989	A4	10/2008
WO	2009063496	A2	5/2009
WO	2009063496	A3	5/2009
WO	2010023621	A2	3/2010
WO	2010023628	A1	3/2010
WO	20100023621	A3	3/2010

OTHER PUBLICATIONS

Foreign communication from a related counterpart application—Intention to Grant, European Patent Application No. 09787015.8, Mar. 27, 2014, 48 pages.

Office Action (Final) dated May 22, 2014 (24 pages), U.S. Appl. No. 12/593,622 filed on Sep. 9, 2009.

Advisory Action dated Aug. 8, 2013 (4 pages), U.S. Appl. No. 12/677,791 filed on Mar. 11, 2010.

Foreign communication from a related counterpart application—International Search Report and Written Opinion, PCT/IN2008/000586, Aug. 24, 2009, 6 pages.

Foreign communication from a related counterpart application—International Search Report and Written Opinion, PCT/IN2008/000586, Mar. 16, 2010, 5 pages.

Foreign communication from a related counterpart application—International Search Report and Written Opinion, PCT/IB2009/053736, Feb. 9, 2010, 11 pages.

Foreign communication from a related counterpart application—International Search Report and Written Opinion, PCT/IB2009/053736, Oct. 18, 2010, 20 pages.

Foreign communication from a related counterpart application—International Search Report and Written Opinion, PCT/IB2009/053726, Jun. 17, 2010, 15 pages.

Foreign communication from a related counterpart application—International Search Report and Written Opinion, PCT/IB2009/053726, Dec. 7, 2010, 14 pages.

Foreign communication from a related counterpart application—International Search Report and Written Opinion, PCT/IN 2008/000217, Mar. 23, 2009, 8 pages.

Foreign communication from a related counterpart application—International Search Report and Written Opinion, PCT/IN2008/000217, Oct. 6, 2009, 7 pages.

Foreign communication from a related counterpart application—International Search Report and Written Opinion, PCT/IN2008/000195, Mar. 25, 2009, 7 pages.

Foreign communication from a related counterpart application—International Search Report and Written Opinion, PCT/IN2008/000195, Oct. 6, 2009, 5 pages.

Office Action dated Oct. 11, 2013 (17 pages), U.S. Appl. No. 12/593,622 filed on Sep. 29, 2009.

Office Action (Final) dated Mar. 19, 2013 (16 pages), U.S. Appl. No. 12/593,622 filed on Sep. 29, 2009.

Office Action dated Jul. 23, 2012 (16 pages), U.S. Appl. No. 12/593,622 filed on Sep. 29, 2009.

Office Action (Restriction Requirement) dated May 2, 2012 (7 pages), U.S. Appl. No. 12/593,622 filed on Sep. 29, 2009.

Office Action (Final) dated Sep. 5, 2013 (13 pages), U.S. Appl. No. 13/061,045 filed on Feb. 25, 2011.

Office Action dated Jan. 29, 2013 (40 pages), U.S. Appl. No. 13/061,045 filed on Feb. 25, 2011.

Office Action (Restriction Requirement) dated Dec. 7, 2012 (7 pages), U.S. Appl. No. 13/061,045 filed on Feb. 25, 2011.

Office Action (Final) dated May 23, 2013 (12 pages), U.S. Appl. No. 12/677,791 filed on Mar. 11, 2010.

Office Action dated Nov. 15, 2012 (14 pages); U.S. Appl. No. 12/677,791 filed on Mar. 11, 2010.

Office Action (Restriction Requirement) dated Jul. 26, 2012 (6 pages), U.S. Appl. No. 12/677,791 filed on Mar. 11, 2010.

Abou, El Naga, H. H., et al., "Succinimide Phosphoric Acid Esters as Multipurpose Additives," XP002565966, Lubrication Science, Jul. 1994, pp. 351-361, vol. 6, No. 4.

Office Action dated Apr. 3, 2014 (20 pages), U.S. Appl. No. 13/061,045 filed on Feb. 25, 2011.

* cited by examiner

NAPHTHENIC ACID CORROSION INHIBITION USING NEW SYNERGETIC COMBINATION OF PHOSPHORUS COMPOUNDS

CROSS-REFERENCE TO RELATED APPLICATIONS

This Application is a U.S. national phase application filed under 35 U.S.C. §371 of International Application No. PCT/IN2008/000217, filed Apr. 3, 2008, designating the United States, which claims priority from Indian Patent Application No.: 676/MUM/2007, filed Apr. 4, 2007, which are hereby incorporated herein by reference in their entirety for all purposes.

FIELD OF THE INVENTION

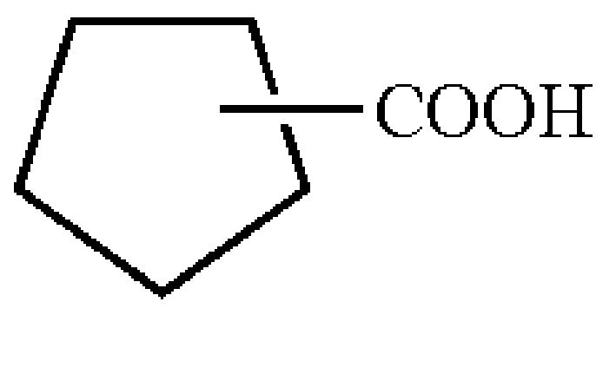
The present invention relates to the inhibition of metal corrosion in acidic hot hydrocarbons and more particularly to the inhibition of corrosion of iron—containing metals in hot acidic hydrocarbons, especially when the acidity is derived from the presence of naphthenic acid. The invention is also useful for sulphur corrosion inhibition.

DISCUSSION OF PRIOR ART

It is widely known in the art that the processing of crude oil and its various fractions has led to damage to piping and other associated equipment due to naphthenic acid corrosion. These are corrosive to the equipment used to distill, extract, transport and process the crudes. Generally speaking, naphthenic acid corrosion occurs when the crude being processed has a neutralization number or total acid number (TAN), expressed as the milligrams of potassium hydroxide required to neutralize the acids in a one gram sample, above 0.2. It is also known that naphthenic acid-containing hydrocarbon is at a temperature between about 200° C. and 400° C. (approximately 400° F.-750° F.), and also when fluid velocities are high or liquid impinges on process surfaces e.g. in transfer lines, return bends and restricted flow areas.

Corrosion problems in petroleum refining operations associated with naphthenic acid constituents and sulfur compounds in crude oils have been recognized for many years. Such corrosion is particularly severe in atmospheric and vacuum distillation units at temperatures between 400° F. and 790° F. Other factors that contribute to the corrosivity of crudes containing naphthenic acids include the amount of naphthenic acid present, the concentration of sulfur compounds, the velocity and turbulence of the flow stream in the units, and the location in the unit (e.g., liquid/vapor interface).

As commonly used, naphthenic acid is a collective term for certain organic acids present in various crude oils. Although there may be present minor amounts of other organic acids, it is understood that the majority of the acids in naphthenic based crude are naphthenic in character, i.e., with a saturated ring structure as follows:



The molecular weight of naphthenic acid can extend over a large range. However, the majority of the naphthenic acid from crude oils is found in gas oil and light lubricating oil. When hydrocarbons containing such naphthenic acid contact iron-containing metals, especially at elevated temperatures, severe corrosion problems arise.

Naphthenic acid corrosion has plagued the refining industry for many years. This corroding material consists of predominantly monocyclic or bicyclic carboxylic acids with a boiling range between 350° and 650° F. These acids tend to concentrate in the heavier fractions during crude distillation. Thus, locations such as the furnace tubing, transfer lines, fractionating tower internals, feed and reflux sections of columns, heat exchangers, tray bottoms and condensers are primary sites of attack for naphthenic acid. Additionally, when crude stocks high in naphthenic acids are processed, severe corrosion can occur in the carbon steel or ferritic steel furnace tubes and tower bottoms. Recently interest has grown in the control of this type of corrosion in hydrocarbon processing units due to the presence of naphthenic acid in crudes from locations such as China, India, Africa and Europe.

Crude oils are hydrocarbon mixtures which have a range of molecular structures and consequent range of physical properties. The physical properties of naphthenic acids which may be contained in the hydrocarbon mixtures also vary with the changes in molecular weight, as well as the source of oil containing the acid. Therefore, characterization and behavior of these acids are not well understood. A well known method used to "quantify" the acid concentration in crude oil has been a KOH titration of the oil. The oil is titrated with KOH, a strong base, to an end point which assures that all acids in the sample have been neutralized. The unit of this titration is mg. of KOH/gram of sample and is referred to as the "Total Acid Number" (TAN) or Neutralization Number. Both terms are used interchangeably in the application.

The unit of TAN is commonly used since it is not possible to calculate the acidity of the oil in terms of moles of acid, or any other of the usual analytical terms for acid content. Refiners have used TAN as a general guideline for predicting naphthenic acid corrosion. For example, many refineries blend their crude to a TAN=0.5 assuming that at these concentrations naphthenic acid corrosion will not occur. However, this measure has been unsuccessful in preventing corrosion by naphthenic acid.

Naphthenic acid corrosion is very temperature dependent. The generally accepted temperature range for this corrosion is between 205° C. and 400° C. (400° F. and 750° F.). Corrosion attack by these acids below 205° C. has not yet been reported in the published literature. As to the upper boundary, data suggests that corrosion rates reach a maximum at about 600°-700° F. and then begin to diminish.

The concentration and velocity of the acid/oil mixture are also important factors which influence naphthenic acid corrosion. This is evidenced by the appearance of the surfaces affected by naphthenic acid corrosion. The manner of corrosion can be deduced from the patterns and color variations in the corroded surfaces. Under some conditions, the metal surface is uniformly thinned. Thinned areas also occur when condensed acid runs down the wall of a vessel. Alternatively, in the presence of naphthenic acid pitting occurs, often in piping or at welds. Usually the metal outside the pit is covered with a heavy, black sulfide film, while the surface of the pit is bright metal or has only, a thin, grey to black film covering it. Moreover, another pattern of corrosion is erosion-corrosion, which has a characteristic pattern of gouges with sharp edges. The surface appears clean, with no visible by-products. The pattern of metal corrosion is indicative of the fluid flow within the system, since increased contact with surfaces allows for a greater amount of corrosion to take place. Therefore, corrosion patterns provide information as to the method of corrosion which has taken place. Also, the more complex the corrosion, i.e., in increasing complexity from uniform to pitting to erosion-corrosion, the lower is the TAN value which triggers the behavior.

The information provided by corrosion patterns indicates whether naphthenic acid is the corroding agent, or rather if the process of corrosion occurs as a result of attack by sulfur. Most crude contain hydrogen sulfide, and therefore readily form iron sulfide films on carbon steel. In all cases that have been observed in the laboratory or in the field, metal surfaces have been covered with a film of some sort. In the presence of hydrogen sulfide the film formed is invariably iron sulfide, while in the few cases where tests have been run in sulfur free conditions, the metal is covered with iron oxide, as there is always enough water or oxygen present to produce a thin film on the metal coupons.

Tests utilized to determine the extent of corrosion may also serve as indicators of the type of corrosion occurring within a particular hydrocarbon treating unit. Metal coupons can be inserted into the system. As they are corroded, they lose material. This weight loss is recorded in units of mg/cm-.sup.2. Thereafter, the corrosion rate can be determined from weight loss measurements. Then the ratio of corrosion rate to corrosion product (mpy/mg/cm.sup.2) is calculated. This is a further indicator of the type of corrosion process which has taken place, for if this ratio is less than 10, it has been found that there is little or no contribution of naphthenic acid to the corrosion process. However, if the ratio exceeds 10, then naphthenic acid is a significant contributor to the corrosion process.

Distinguishing between sulfidation attack and corrosion caused by naphthenic acid is important, since different remedies are required depending upon the corroding agent. Usually, retardation of corrosion caused by sulfur compounds at elevated temperatures is effected by increasing the amount of chromium in the alloy which is used in the hydrocarbon treating unit. A range of alloys may, be employed, from 1.25% Cr to 12% Cr, or perhaps even higher. Unfortunately, these show little to no resistance to naphthenic acid. To compensate for the corroding effects of sulfur and naphthenic acid, an austenitic stainless steel which contains at least 2.5% molybdenum, must be utilized. The corrosive problem is known to be aggravated by the elevated temperatures necessary to refine and crack the oil and by the oil's acidity which is caused primarily by high levels of naphthenic acid indigenous to the crudes. Naphthenic acids is corrosive between the range of about 175° C. to 420° C. At the higher temperatures the naphthenic acids are in the vapor phase and at the lower temperatures the corrosion rate is not serious. The corrosivity of naphthenic acids appears to be exceptionally serious in the presence of sulfide compounds, such as hydrogen sulfide, mercaptans, elemental sulfur, sulfides, disulfides, polysulfides and thiophenols. Corrosion due to sulfur compounds becomes significant at temperatures as low as 450° F. The catalytic generation of hydrogen sulfide by thermal decomposition of mercaptans has been identified as a cause of sulfidic corrosion.

Sulfur in the crudes, which produces hydrogen sulfide at higher temperatures, also aggravates the problem. The temperature range of primary interest for this type of corrosion is in the range of about 175° C. to about 400° C., especially about 205° C. to about 400° C.

Various approaches to controlling naphthenic acid corrosion have included neutralization and/or removal of naphthenic acids from the crude being processed; blending low acid number oils with corrosive high acid number oils to reduce the overall neutralization number; and the use of relatively expensive corrosion-resistant alloys in the construction of the piping and associated equipment. These attempts are generally disadvantageous in that they require additional processing and/or add substantial costs to treatment of the crude oil. Alternatively, various amine and amide based corrosion inhibitors are commercially available, but these are generally ineffective in the high temperature environment of naphthenic acid corrosion. Naphthenic acid corrosion is readily distinguished from conventional fouling problems such as coking and polymer deposition which can occur in ethylene cracking and other hydrocarbon processing reactions using petroleum based feedstocks. Naphthenic acid corrosion produces a characteristic grooving of the metal in contact with the corrosive stream. In contrast, coke deposits generally have corrosive effects due to carburization, erosion and metal dusting.

Because these approaches have not been entirely satisfactory, the accepted approach in the industry is to construct the distillation unit, or the portions exposed to naphthenic acid/sulfur corrosion, with the resistant metals such as high quality stainless steel or alloys containing higher amounts of chromium and molybdenum. The installation of corrosion-resistant alloys is capital intensive, as alloys such as 304 and 316 stainless steels are several times the cost of carbon steel. However, in units not so constructed there is a need to provide inhibition treatment against this type of corrosion. The prior art corrosion inhibitors for naphthenic acid environments include nitrogen-based filming corrosion inhibitors. However, these corrosion inhibitors are relatively ineffective in the high temperature environment of naphthenic acid oils.

While various corrosion inhibitors are known in various arts, the efficacy and usefulness of any particular corrosion inhibitor is dependent on the particular circumstances in which it is applied. Thus, efficacy or usefulness under one set of circumstances often does not imply the same for another set of circumstances. As a result, a large number of corrosion inhibitors have been developed and are in use for application to various systems depending on the medium treated, the type of surface that is susceptible to the corrosion, the type of corrosion encountered, and the conditions to which the medium is exposed. For example, U.S. Pat. No. 3,909,447 describes certain corrosion inhibitors as useful against corrosion in relatively low temperature oxygenated aqueous systems such as water floods, cooling towers, drilling muds, air drilling and auto radiator systems. That patent also notes that many corrosion inhibitors capable of performing in non-aqueous systems and/or non-oxygenated systems perform poorly in aqueous and/or oxygenated systems. The reverse is true as well. The mere fact that an inhibitor that has shown efficacy in oxygenated aqueous systems does not suggest that it would show efficacy in a hydrocarbon. Moreover, the mere fact that an inhibitor has been efficacious at relatively low temperatures does not indicate that it would be efficacious at elevated temperatures. In fact, it is common for inhibitors that are very effective at relatively low temperatures to become ineffective at temperatures such as the 175° C. to 400° C. encountered in oil refining. At such temperatures, corrosion is notoriously troublesome and difficult to alleviate. Thus, U.S. Pat. No. 3,909,447 contains no teaching or suggestion that it would be effective in non-aqueous systems such as hydrocarbon fluids, especially hot hydrocarbon fluids. Nor is there any indication in U.S. Pat. No. 3,909,447 that the compounds disclosed therein would be effective against naphthenic acid corrosion under such conditions.

Atmospheric and vacuum distillation systems are subject to naphthenic acid corrosion when processing certain crude oils. Currently used treatments are thermally reactive at use temperatures. In the case of phosphorus-based inhibitors, this is thought to lead to a metal phosphate surface film. The film is more resistant to naphthenic acid corrosion than the base steel. These inhibitors are relatively volatile and exhibit fairly narrow distillation ranges. They are fed into a column above or below the point of corrosion depending on the temperature range. Polysulfide inhibitors decompose into complex mixtures of higher and lower polysulfides and, perhaps, elemental sulfur and mercaptans. Thus, the volatility and protection offered is not predictable.

The problems caused by naphthenic acid corrosion in refineries and the prior art solutions to that problem have been described at length in the literature, the following of which are representative:

U.S. Pat. No. 3,531,394 to Koszman described the use of phosphorus and/or bismuth compounds in the cracking zone of petroleum steam furnaces to inhibit coke formation on the furnace tube walls.

U.S. Pat. No. 4,024,049 to Shell et al discloses compounds substantially as described and claimed herein for use as refinery antifoulants. While effective as antifoulant materials, materials of this type have not heretofore been used as corrosion inhibitors in the manner set forth herein. While this reference teaches the addition of thiophosphate esters such as those used in the subject invention to the incoming feed, due to the non-volatile nature of the ester materials they do not distill into the column to protect the column, the pump around piping, or further process steps. I have found that by injecting the thiophosphate esters as taught herein, surprising activity is obtained in preventing the occurrence of naphthenic acid corrosion in distillation columns, pump around piping, and associated equipment.

U.S. Pat. No. 4,105,540 to Weinland describes phosphorus containing compounds as antifoulant additives in ethylene cracking furnaces. The phosphorus compounds employed are mono- and di-ester phosphate and phosphite compounds having at least one hydrogen moiety complexed with an amine.

U.S. Pat. No. 4,443,609 discloses certain tetrahydrothiazole phosphonic acids and esters as being useful as acid corrosion inhibitors. Such inhibitors can be prepared by reacting certain 2, 5-dihydrothiazoles with a dialkyl phosphite. While these tetrahydrothiazole phosphonic acids or esters have good corrosion and inhibition properties, they tend to break down during high temperature applications thereof with possible emission of obnoxious and toxic substances.

It is also known that phosphorus-containing compounds impair the function of various catalysts used to treat crude oil, e.g., in fixed-bed hydrotreaters and hydrocracking units. Crude oil processors are often in a quandary since if the phosphite stabilizer is not used, then iron can accumulate in the hydrocarbon up to 10 to 20 ppm and impair the catalyst. Although nonphosphorus-containing inhibitors are commercially available, they are generally less effective than the phosphorus-containing compounds.

U.S. Pat. No. 4,542,253 to Kaplan et al, described an improved method of reducing fouling and corrosion in ethylene cracking furnaces using petroleum feedstocks including at least 10 ppm of a water soluble mine complexed phosphate, phosphite, thiophosphate or thiophosphite ester compound, wherein the amine has a partition coefficient greater than 1.0 (equal solubility in both aqueous and hydrocarbon solvents).

U.S. Pat. No. 4,842,716 to Kaplan et al describes an improved method for reducing fouling and corrosion at least 10 ppm of a combination of a phosphorus antifoulant compound and a filming inhibitor. The phosphorus compound is a phosphate, phosphite, thiophosphate or thiophosphite ester compound. The filming inhibitor is an imidazoline compound.

U.S. Pat. No. 4,941,994 Zetmeisl et al discloses a naphthenic acid corrosion inhibitor comprising a dialkyl or trialkylphosphite in combination with an optional thiazoline.

A significant advancement in phosphorus-containing naphthenic acid corrosion inhibitors was reported in U.S. Pat. No. 4,941,994. Therein it is disclosed that metal corrosion in hot acidic liquid hydrocarbons is inhibited by the presence of a corrosion inhibiting amount of a dialkyl and/or trialkyl phosphite with an optional thiazoline.

While the method described in U.S. Pat. No. 4,941,994 provides significant improvements over the prior art techniques, nevertheless, there is always a desire to enhance the ability of corrosion inhibitors while reducing the amount of phosphorus-containing compounds which may impair the function of various catalysts used to treat crude oil, as well as a desire for such inhibitors that may be produced from lower cost or more available starting materials.

Another approach to the prevention of naphthenic acid corrosion is the use of a chemical agent to form a barrier between the crude and the equipment of the hydrocarbon processing unit. This barrier or film prevents corrosive agents from reaching the metal surface, and is generally a hydrophobic material.

Gustaysen et al. NACE Corrosion 89 meeting, paper no. 449, Apr. 17-21, 1989 details the requirements for a good filming agent. U.S. Pat. No. 5,252,254 discloses one such film forming agent, sulfonated alkyl-substituted phenol, and effective against naphthenic acid corrosion.

U.S. Pat. No. 5,182,013 issued to Petersen et al. on Jan. 26, 1993 describes another method of inhibiting naphthenic acid corrosion of crude oil, comprising introducing into the oil an effective amount of an organic polysulfide. The disclosure of U.S. Pat. No. 5,182,013 is incorporated herein by reference. This is another example of a corrosion-inhibiting sulfur species. Sulfidation as a source of corrosion was detailed above. Though the process is not well understood, it has been determined that while sulfur can be an effective anti-corrosive agent in small quantities, at sufficiently high concentrations, it becomes a corrosion agent.

Phosphorus can form an effective barrier against corrosion without sulfur, but the addition of sulfiding agents to the process stream containing phosphorus yields a film composed of both sulfides and phosphates. This results in improved performance as well as a decreased phosphorus requirement. This invention pertains to the deliberate addition of sulfiding agents to the process stream when phosphorus-based materials are used for corrosion control to accentuate this interaction.

U.S. Pat. No. 5,314,643 to Edmondson et al., describes a process for inhibition of corrosion caused by naphthenic acid and sulphur compounds during the elevated temperature processing of crude oil by use of a corrosion inhibitor consisting of a combination of trialkylphosphate and an alkaline earth metal phosphonate-phenate sulphide, functioning effectively as an inhibitor on the internal metallic surfaces of the equipment used in crude oil refining operations.

Organic polysulfides (Babaian-Kibala, U.S. Pat. No. 5,552,085), organic phosphites (Zetlmeisl, U.S. Pat. No. 4,941,994), and phosphate/phosphite esters (Babaian-Kibala, U.S. Pat. No. 5,630,964), have been claimed to be effective in hydrocarbon-rich phase against naphthenic acid corrosion. However, their high oil solubility incurs the risk of distillate side stream contamination by phosphorus.

Phosphoric acid has been used primarily in aqueous phase for the formation of a phosphate/iron complex film on steel surfaces for corrosion inhibition or other applications (Coslett, British patent 8,667, U.S. Pat. Nos. 3,132,975, 3,460,989 and 1,872,091). Phosphoric acid use in high temperature non-aqueous environments (petroleum) has also been reported for purposes of fouling mitigation (U.S. Pat. No. 3,145,886).

There remains a continuing need to develop additional options for mitigating the corrosivity of acidic crudes at lower cost. This is especially true at times of low refining margins and a high availability of corrosive crudes from sources such as Europe, China, or Africa, and India. The present invention addresses this need.

OBJECTS AND ADVANTAGES OF PRESENT INVENTION

Accordingly, the objects and advantages of the present invention are described below.

An object of present invention is to provide a chemical composition which will provide very effective high temperature naphthenic acid corrosion inhibition as well as sulphur corrosion inhibition.

Another object of the present invention is to provide a corrosion inhibiting composition, which is very stable even at high temperature.

Yet another object of the present invention is to provide a corrosion inhibiting composition, having very low acid value.

SUMMARY OF INVENTION

The present invention relates to the field of processing hydrocarbons which causes corrosion in the metal surfaces of processing units. The invention addresses the technical problem of high temperature naphthenic acid corrosion and sulphur corrosion and provides a solution to inhibit these types of corrosion. The three combination compositions are formed by three mixtures separately, with one mixture obtained by mixing compound A, which is obtained by reacting high reactive polyisobutylene (HRPIB) with phosphorous pentasulphide in presence of catalytic amount of sulphur with compound B such as trialkyl phosphate and second mixture obtained by mixing compound A with compound C such as phosphite like di-isodecyl phenyl phosphite, and third mixture obtained by mixing compound A with compound D such as a phosphonate, wherein each of these three mixtures independently provide high corrosion inhibition efficiency in case of high temperature naphthenic acid corrosion inhibition and sulphur corrosion inhibition. The invention is useful in all hydrocarbon processing units, such as, refineries, distillation columns and other petrochemical industries.

DESCRIPTION OF THE INVENTION

It has been surprisingly discovered by the inventor of the present invention, that a combination of organophosphorus sulphur compound and any of other phosphorus compounds such as, phosphates, phosphites and phosphonates, is very efficiently functioning in controlling naphthenic acid corrosion, providing a synergetic effect of combination of Phosphorus compounds. The organophosphorus sulphur compound is made from reaction of hydrocarbon R_1 such as olefins with, phosphorus pentasulphide, in presence of sulphur powder. Amongst the other Phosphorus compounds tributylphosphate and di-isodecyl phenyl phosphite are the preferred ones.

The preferred olefins have double bonds, wherein double bond is present internally or terminally. The details about such hydrocarbon R_1 are given below:

As previously mentioned, the term “hydrocarbon” as used herein means any one of an alkyl group, an alkenyl group, an alkynyl group, which groups may be linear, branched or cyclic, or an aryl group. The term hydrocarbon also includes those groups but wherein they have been optionally substituted. If the hydrocarbon is a branched structure having substituent(s) thereon, then the substitution may be on either the hydrocarbon backbone or on the branch; alternatively the substitutions may be on the hydrocarbon backbone and on the branch.

Preferably R_1 is an optionally substituted alkyl or alkenyl group. In one aspect R_1 is an optionally substituted alkyl group. In another aspect, R_1 is an optionally substituted alkenyl group.

The term “alkenyl” refers to a branched or straight chain hydrocarbon, which can comprise one or more carbon-carbon double bonds. Exemplary alkenyl groups include propylenyl, butenyl, isobutenyl, pentenyl, 2,2-methylbutenyl, 3-methylbutenyl, hexanyl, heptenyl, octenyl, and polymers thereof.

In one aspect R_1 is an optionally substituted branched alkyl or alkenyl group. Preferably, R_1 is a polyisobutenyl (PIB) group.

Conventional PIBs and so-called “high-reactivity” PIBs (see for example EP-B-0565285) are suitable for use in this invention. High reactivity in this context is defined as a PIB wherein at least 50%, preferably 70% or more, of the terminal olefinic double bonds are of the vinylidene type, for example the GLISSOPAL compounds available from BASF.

In one aspect R_1 has between 10 and 1000 carbon atoms, preferably between 4 and 200 carbon atoms.

In one aspect, R_1 has a molecular weight of from 200 to 10000, preferably from 200 to 1300.

The trialkylphosphate such as tributyl phosphate will contain an alkyl moiety of C_1-C_{12} such that those compounds contemplated as having the desired efficacy and within the disclosure of the present invention include trimethylphosphate, triethylphosphate, tripropylphosphate, tributylphosphate and tripentylphosphate. Due to its easy commercial availability, tributylphosphate may be considered the preferred compound.

The most effective amount of the corrosion inhibitor to be used in accordance with the present invention can vary depending on the local operating conditions and the particular hydrocarbon being processed. Thus, the temperature and other characteristics of the acid corrosion system can have a bearing on the amount of inhibitor or mixture of inhibitors to be used. Generally, where the operating temperatures and/or the acid concentrations are higher, a proportionately higher amount of the corrosion inhibitor will be required. It has been found that the concentration of the corrosion inhibitors or mixture of inhibitors added to the crude oil may range from about 1 ppm to 5000 ppm. It has also been found that it is preferred to add the inhibitors at a relatively high initial dosage rate of 2000-3000 ppm and to maintain this level for a relatively short period of time until the presence of the inhibitor induces the build-up of a corrosion protective coating on the metal surfaces.

Once the protective surface is established, the dosage rate needed to maintain the protection may be reduced to a normal operational range of about 100-1500 ppm without substantial sacrifice of protection.

The inventor of the present invention has carried out extensive experimentation to verify the effectiveness of corrosion—inhibition in case naphthenic acid corrosion, by experimenting with different proportions of compound A, that is, polyisobutylene plus phosphorus pentasulphide plus sulphur powder and compound B, that is, tributyl phosphate in the abovementioned combination of these compounds. Experiments were also preformed by using compound A alone and compound B alone separately.

The inventor of the present invention has also carried out extensive experimentation to verify the effectiveness of corrosion—inhibition in case of naphthenic acid corrosion, by experimenting with different proportions of compound A, that is, polyisobutylene plus phosphorus pentasulphide plus sulphur powder and compound C, that is, di-isodecyl phenyl phosphite in the abovementioned combination of these compounds. Experiments were also preformed by using compound A alone and compound B alone and compound C alone, separately.

The reacted compound "A" is obtained by reaction of olefins with P_2S_5 (Phosphorus pentasulphide) in presence of sulphur powder. The preferred olefins have double bonds, wherein double bond is present internally or terminally.

The example of internally double bonded olefins include beta-olefins.

The example of terminally double bonded olefins include alpha-olefins. These olefins have 5 to 30 carbon atoms. These olefins are alternatively, polymeric olefins such as high reactive polyisobutylene containing greater than 70% of vinyledene double bond, and normal polyisobutylene which contains Vinyl, vinyledene, and such other groups of chemicals.

The ratio of P_2S_5 to Olefin is preferably 0.05 to 2 mole of P_2S_5 to 1 mole of Olefins. The Sulphur powder is present in catalytic quantity, that is, sulphur powder is 0.5% to 5% of Olefin by weight.

The most preferred embodiment of the present invention is described below: A weighed quantity of HRPIB (High Reactive Polyisobutylene), Phosphorus pentasulphide and sulphur powder are charged into a clean four-necked round bottom flask, equipped with nitrogen inlet, stirrer and thermometer, thereby forming a reaction mixture.

This reaction mixture is stirred and heated to temperature of 160° C. under nitrogen gas purging. At this temperature of 160° C., the reaction leads to evolution of hydrogen sulphide gas (H_2S). The temperature of the reaction mixture is now maintained between 160° C. to 180° C., for a period of 1 hour to 2 hours. Then the temperature of the mixture is raised to 220° C. The reaction mixture is then maintained at this temperature of 220° C. for 6 hours.

This reaction mixture is stirred and heated to temperature of 160° C. under nitrogen gas purging. At this temperature of 160° C., the reaction leads to evolution of hydrogen sulphide gas (H_2S). The temperature of the reaction mixture is now maintained between 160° C. to 180° C., for a period of 1 hour to 2 hours. Then the temperature of the mixture is raised to 220° C. The reaction mixture is then maintained at this temperature of 220° C. for 6 hours.

The present invention is directed to a method for inhibiting corrosion on the metal surfaces of the processing units which process hydrocarbons such as crude oil and its fractions containing naphthenic acid. The invention is explained in details in its simplest form wherein the following method steps are carried out, when it is used to process crude oil in process units such as distillation unit. Similar steps can be used in different processing units such as, pump around piping, heat exchangers and such other processing units.

These method steps are explained below:

a) heating the hydrocarbon containing naphthenic acid to vaporize a portion of the hydrocarbon;
b) allowing the hydrocarbon vapors to rise in a distillation column;
c) condensing a portion of the hydrocarbon vapours passing through the distillation column to produce a distillate;
d) adding to the distillate, from 1 to 5000 ppm of a combination compound (A+B) or combination compound (A+C) of instant invention;
e) allowing the distillate containing combination compound (A+B) or combination compound (A+C) to contact substantially the entire metal surfaces of the distillation unit to form protective film on such surface, whereby such surface is inhibited against corrosion.

It is advantageous to treat distillation column, trays, pump around piping and related equipment to prevent naphthenic acid corrosion, when condensed vapours from distilled hydrocarbon fluids contact metallic equipment at temperatures greater than 200° C., and preferably 400° C. The combination compound (A+B) or combination compound (A+C) as additive is generally added to the condensed distillate and the condensed distillate is allowed to contact the metallic surfaces of the distillation column, packing, trays, pump around piping and related equipment as the condensed distillate passes down the column and into the distillation vessel. The distillate may also be collected as product. The corrosion inhibitors of the instant invention remain in the resultant collected product.

In commercial practice, the additives of this invention may be added to a distillate return to control corrosion in a draw tray and in the column packing while a second injection may be added to a spray oil return immediately below the draw trays to protect the tower packing and trays below the distillate draw tray. It is not so critical where the additive of the invention is added as long as it is added to distillate that is later returned to the distillation vessel, or which contact the metal interior surfaces of the distillation column, trays, pump around piping and related equipments.

The method of using the polyisobutylene phosphorus sulphur compound of the present invention for achieving inhibition of high temperature naphthenic acid corrosion is explained below with the help of examples 1 and 2.

Example 3 shows use of compound B.

Example 4 shows use of combination compound (A+B).

Example 5 shows use of compound C.

Example 6 shows use of combination compound (A+C).

The compound B of the combination compound (A+B) of the present invention is easily obtained commercially.

The compound C of the combination compound (A+C) of the present invention is easily obtained commercially.

EXAMPLE 1

The weighed quantities of 68.16 gm of commercially available HRPIB (High Reactive Polyisobutylene with molecular weight 950 approximately), 30.31 gm of Phosphorus Pentasulphide and 1.51 gm of Sulphur Powder are charged into a clean four necked round bottom flask, equipped with N_2 inlet, stirrer and thermometer, thereby forming a reaction mixture. This gives 1:1 mole ratio of Phosphorus Pentasulphide to Olefin.

The reaction mixture was stirred and heated to 160° C. temperature under nitrogen gas purging. The purging of N_2 gas led to removal of hydrogen sulphide gas, which was generated during the reaction. The temperature of the reaction mixture was maintained between 160° C. to 180° C., for a period of 1 hour to 2 hours. Then the temperature of the mixture was raised to 220° C. and the mixture was maintained at this temperature for 6 to 10 hours.

The resultant reaction mass was then cooled to 100° C. when nitrogen gas was purged into it, to drive out the hydrogen sulphide gas present therein. The resulting polyisobutylene Phosphorus sulphur compound was used as a high temperature naphthenic acid corrosion inhibitor, as well as, sulphur corrosion inhibitor. This compound was used neat or diluted in appropriate solvent such as xylene, toluene, and aromatic solvent as well as any other appropriate solvent to achieve inhibition of high temperature naphthenic acid corrosion as well as sulphur corrosion.

The above mentioned synthesis is carried out for different molar ratios of 1:1, 1:0.5 and 1:0.25 of HRPIB to Phosphorus Pentasulphide. A similar synthesis was carried out by using normal polyisobutylene instead of HRPIB, with molar ratio of 1:0.35.

EXAMPLE 2

High Temperature Naphthenic Acid Corrosion Test

In this example, various amounts of a 50% formulation of the composition prepared in accordance, with Example 1, were tested for corrosion inhibition efficiency on steel coupons in hot oil containing naphthenic acid. A weight loss coupon, immersion test was used to evaluate the invention compound for its effectiveness in inhibition of naphthenic acid corrosion at 290° C. temperature. Different dosage such as 300, 400 and 600 ppm of invention compound were used, as 50% active solution.

A corrosion inhibition test on steel coupon was conducted without using any additive. This test provided a blank test reading.

The reaction apparatus consisted of a one-litre four necked round bottom flask equipped with water condenser, N_2 purger tube, thermometer pocket with thermometer and stirrer rod. 600 gm (about 750 ml) paraffin hydrocarbon oil (D-130) was taken in the flask. N_2 gas purging was started with flow rate of 100 cc/minute and the temperature was raised to 100° C., which temperature was maintained for 30 minutes. A compound of example 1 comprising Polyisobutylene and Phosphorus Pentasulphide with sulphur powder was added to the reaction mixture. The reaction mixture was stirred for 15 minutes at 100° C. temperature. After removing the stirrer, the temperature of the reaction mixture was raised to 290° C. A pre-weighed weight-loss carbon steel coupon CS 1010 with dimensions 76 mm×13 mm×1.6 mm was immersed. After maintaining this condition for 1 hour to 1.5 hours, 31 gm of naphthenic acid (commercial grade with acid value of 230 mg/KOH) was added to the reaction mixture. A sample of one gm weight of reaction mixture was collected for determination of acid value, which was found to be approximately 11.7. This condition was maintained for four hours. After this procedure, the metal coupon was removed, excess oil was rinsed away, and the excess corrosion product was removed from the metal surface. Then the metal coupon was weighed and the corrosion rate was calculated in mils per year.

Calculation of Corrosion Inhibition Efficiency.

The method used in calculating Corrosion Inhibition Efficiency is given below. In this calculation, corrosion inhibition efficiency provided by additive compound is calculated by comparing weight loss due to additive with weight loss of blank coupon (without any additive).

$$\text{Corrosion Inhibition Efficiency} = \frac{(\text{Weight loss for blank without additive}) - (\text{weight loss with additive})}{(\text{weight loss for blank without additive})} \times 100$$

The calculated magnitudes are entered in the Tables in appropriate columns.

The results of the experiments are presented in Table I and II.

The test results of the experiments conducted by using normal polyisobutylene are given in Table III.

The corrosion rate in MPY (mils per year) is calculated by the formula,

$$MPY = \frac{534 \times \text{Weight loss in mg}}{(\text{Density in gm/cc}) \times (\text{Area in in}^2) \times (\text{Time of test in hours})}$$

EXAMPLE 3

Experiments were carried out by the inventor of the present invention, to test the effectiveness of a commercially available phosphorus compound B, such as tributyl phosphate, in inhibition of naphthenic acid corrosion. Different dosages of tributyl phosphate, such as 75, 90 and 100 ppm were used in the experiments. The result of some of these experiments are presented in Table 5.

EXAMPLE 4

Experiments were carried out by the inventor of the present invention, to test the synergetic effectiveness of a combination of the compounds A and B, where compound A represents high reactive polyisobutylene plus Phosphorus pentasulphide plus sulphur powder and compound B represents tributyl phosphate (compound B is used as available commercially). Different total dosages of inhibitor combination compound's combination such as 300 ppm and 400 ppm were used in the experimentation. Similarly, different proportions of compound A and compound B, were used in these experiments. These different percentage proportions of A:B were 67:33, 70:30, 75:25, and 81:19. The result of these experiments are presented in Tables 6 to 8.

EXAMPLE 5

By using the method steps similar to that of example 2, the experiments were carried out by the inventor of the present invention, to test the effectiveness of another commercially available Phosphorus compound C, such as Di-isodecyl Phenyl Phosphite, in inhibition of naphthenic acid corrosion. Different active dosages of Di-isodecyl Phenyl Phosphite, such as 75, 90, 120 and 150 ppm were used in the experiments. The results of these experiments are presented in Table 9.

EXAMPLE 6

By using the method steps similar to that of example 5, the experiments were carried out by the inventor of the present invention, to test synergetic effectiveness of a combination of the compounds A and C, in inhibition of naphthenic acid corrosion, where compound A represents high reactive polyisobutylene plus phosphorus pentasulphide plus catalytic amount of sulphur powder and compound C represents Diisodecyl Phenyl Phosphite, (Compound C is used as available commercially). Different total active dosages of inhibitor combination compound's combination such as 195, 200, 210, 250, 300 ppm were used in the experimentation. Similarly these total active dosages included different proportions of active compounds A and C. These different proportions of A:C included 105:90, 90:120, 100:100, 140:60, 110:90, 130:120 and 180:120 the results of these experiments are presented in Table 10.

TABLE 1

CORROSION INHIBITION TEST (with molar ratio of Polyisobutylene to Phosphorus Pentasulphide = 1:1) (EXAMPLE - 2)

Expt. No.	Inhibitor Compound	Dosage in ppm	Effective Dosage in ppm	Weight Loss in mg	Corrosion Rate in MPY	Corrosion Inhibition efficiency in %
1	(Only blank)	—	—	89.5	529.89	0
2	Composition as per Example 1	200	100	63.3	371.23	29.27
3	Composition as per Example 1	300	150	39.6	232.24	55.75
4	Composition as per Example 1	400	200	15.2	89.114	83.02
5	Composition as per Example 1	600	300	3.8	12.31	95.75
6	Composition as per Example 1	650	325	0.3	1.5	99.67

TABLE 2

CORROSION INHIBITION TEST (with molar ratio of Polyisobutylene to Phosphorus Pentasulphide = 1:0.5) (EXAMPLE - 2)

Experiment No.	Inhibitor Compound	Dosage in ppm	Effective Dosage in ppm	Weight Loss in mg	Corrosion Rate in MPY	Corrosion Inhibition Efficiency in %
15	— (Only blank)	—	—	87.7	439	0
7	Composition as per Example 1	500	250	21.5	107.62	75.48

TABLE 3

CORROSION INHIBITION TEST (with molar ratio of Polyisobutylene to Phosphorus Pentasulphide = 1:0.25) (EXAMPLE - 2)

Experiment No.	Inhibitor Compound	Dosage in ppm	Effective Dosage in ppm	Weight Loss in mg	Corrosion Rate in MPY	Corrosion Inhibition efficiency in %
15	— (Only blank)	—	—	87.7	439	0
8	Composition as per Example 1	500	250	50.6	253.3	42.3
9	Composition as per Example 1	1000	500	14.2	71.08	83.81
10	Composition as per Example 1	1500	750	2.0	10.1	97.72

TABLE 4

CORROSION INHIBITION TEST (with molar ratio of Normal Polyisobutylene to Phosphorus Pentasulphide = 1:0.35)

Expt. No.	Inhibitor Compound	Dosage in ppm	Effective Dosage in ppm	Weight Loss in mg	Corrosion Rate in MPY	Corrosion Inhibition efficiency in %
15	— (Only blank)	—	—	87.7	439	0
11	Composition as per Example 1	600	300	40	200.21	54.39

TABLE 5

CORROSION INHIBITION TEST (Inhibitor compound B = Tributyl Phosphate)

Experiment No.	Inhibitor Compound	Dosage in ppm	Weight Loss in mg	Corrosion Rate MPY	Corrosion Inhibition efficiency in %
1	— (Only blank)	—	89.5	529.89	0
12	Tributyl Phosphate (as commercially available) without any solvent	75	55.5	325.49	37.99
13	Compound as per Experiment No 12	90	21.95	128.73	75.48
14	Compound as per Experiment No 12	100	14.35	84.16	83.97

TABLE 6

CORROSION INHIBITION TEST (Inhibitor compound = A + B)

Expt. No.	M.R	Inhibitor compound	Dosage in (ppm) Compound A	Compound B	Total Dosage A + B	Weight loss (mg)	Corrosion Rate in (MPY)	Corrosion Inhibition efficiency (%)
15	—	(Blank)	—	—	—	87.70	439	0
16	1:1	A + B	120	80	200	0	10	100
17	1:1	A + B	150	75	225	2.2	11.01	97.49
18	1:1	A + B	180	60	240	0.7	3.5	99.20

Compound A = 50% of Polyisobutylene plus Phosphorus Pentasulphide + Catalytic amount of Sulphur Powder (as per example 1) and 50% solvent

Compound B = Tributyl Phosphate (as commercially available) without any solvent.

M.R. = Molar Ratio of Polyisobutylene to Phosphorus Pentasulphide

TABLE 7

CORROSION INHIBITION TEST (Inhibitor compound = A + B)

Expt. No.	M.R.	Inhibitor compound	Dosage in (ppm) Compound A	Compound B	Total Dosage A + B	Weight loss (mg)	Corrosion Rate in (MPY)	Corrosion Inhibition efficiency (%)
1	—	(Only blank)	—	—	—	89.5	529.89	0
19	1:1	A + B	200	100	300	2.73	16.01	96.95
20	1:1	A + B	210	90	300	2.90	17.00	96.76
21	1:1	A + B	225	75	300	5.30	31.08	94.08
22	1:1	A + B	325	75	400	4.70	27.56	94.75

Compound A = 50% of Polyisobutylene plus Phosphorus Pentasulphide + Catalytic amount of Sulphur Powder (as per example 1) and 50% solvent

Compound B = Tributyl Phosphate (as commercially available) without any solvent.

M.R. = Molar Ratio of Polyisobutylene to Phosphorus Pentasulphide

TABLE 8

CORROSION INHIBITION TEST (Inhibitor compound = A + B)

			Dosage in (ppm)			Weight	Corrosion.	Corrosion Inhibition
Experiment No.	M.R.	Inhibitor comp.	Comp. A	Comp. B	Total Dosage A + B	loss (mg)	Rate in (MPY)	efficiency (%)
15	—	(Only blank)	—	—	—	87.7	439	0
23	1:0.5	A + B	300	75	375	1.8	9.01	97.95
24	1:0.5	A + B	330	60	390	5.2	26.03	94.07
25	1:0.5	A + B	255	45	300	39.4	197.21	55.07

Compound A = 50% of Polyisobutylene plus Phosphorus Pentasulphide + Catalytic amount of Sulphur Powder (as per example 1) and 50% solvent
Compound B = Tributyl Phosphate (as commercially available) without any solvent.
M.R. = Molar Ratio of Polyisobutylene to Phosphorus Pentasulphide

TABLE 9

CORROSION INHIBITION TEST (Inhibitor compound C = Di-isodecyl Phenyl Phosphite as commercially available without any solvent)

Experiment No.	Inhibitor Compound	Dosage in ppm	Weight Loss in mg	Corrosion Rate in MPY	Corrosion Inhibition efficiency in %
15	(Only blank)	—	87.70	439	0
26	Di-isodecyl Phenyl Phosphite without any solvent	75	73.90	369.90	15.74
27	Compound as per Experiment No 26	90	58.5	292.81	33.30
28	Compound as per Experiment No 26	120	21.0	105.11	76.05
29	Compound as per Experiment No 26	150	1.60	8.01	98.18

TABLE 10

CORROSION INHIBITION TEST (Inhibitor compound = A + C)

			Dosage in (ppm)			Weight	Corrosion	Corrosion Inhibition
Expt. No.	M.R.	Inhibitor compound	Comp. A	Comp. C	Total Dosage A + C	loss (mg)	Rate in (MPY)	efficiency (%)
15	—	(Only blank)	—	—	—	87.7	439	0
30	1:1	A + C	210	90	300	4.9	24.53	94.41
31	1:1	A + C	180	120	300	0.7	3.5	99.20
32	1:1	A + C	200	100	300	0.3	1.5	99.66
33	1:1	A + C	280	60	340	0.4	2.0	99.54
34	1:1	A + C	220	90	310	0.1	0.5	99.89
35	1:0.5	A + C	260	120	380	1.5	7.51	98.29
36	1:0.5	A + C	360	120	480	3.4	17.02	96.12

Compound A = 50% of Polyisobutylene plus Phosphorus Pentasulphide + Catalytic amount of Sulphur Powder (as per example 1) and 50% solvent
Compound C = Di-isodecyl Phenyl Phosphite as commercially available without any solvent

TABLE 11

CORROSION INHIBITION TEST (Inhibitor compound = A + B)

			Dosage in (ppm)			Weight	Corrosion.	Corrosion Inhibition
Expt. No.	M.R.	Inhibitor comp.	Comp. A	Comp. B	Total Dosage A + B	loss (mg)	Rate in (MPY)	efficiency (%)
15	—	(Only blank)	—	—	—	87.7	439	0
37	1:0.35	A + B	320	90	410	1.3	6.5	98.52

Compound A = 50% of Normal Polyisobutylene plus Phosphorus Pentasulphide + Catalytic amount of Sulphur Powder (as per example 1) and 50% solvent
Compound B = Tributyl Phosphate (as commercially available) without any solvent.
M.R. = Molar Ratio of Polyisobutylene to Phosphorus Pentasulphide

TABLE 12

CORROSION INHIBITION TEST (Inhibitor compound = A + C)

Expt. No.	M.R.	Inhibitor compound	Dosage in (ppm) Comp. A	Comp. C	Total Dosage A + C	Weight loss (mg)	Corrosion Rate in (MPY)	Corrosion Inhibition efficiency (%)
15	—	(Only blank)	—	—	—	87.7	439	0
38	1:0.35	A + C	360	120	480	24.2	121	72.41

Compound A = 50% of Normal Polyisobutylene plus Phosphorus Pentasulphide + Catalytic amount of Sulphur Powder (as per example 1) and 50% solvent
Compound C = Di-isodecyl Phenyl Phosphite as commercially available without any solvent

Discussion of the Results Presented in Tables

The detailed discussion given below with respect to the results presented in Tables 1 to 12 for the experiments described in Examples 1 to 6 explains the effectiveness of the additive inhibitor compounds of present invention in high temperature naphthenic acid corrosion inhibition or sulphur corrosion inhibition.

The additive inhibitor compound of the present invention, which is very effective in inhibition of high temperature naphthenic acid corrosion, comprises a mixture of a compound A with either of the two compounds B and C, wherein,

A=50% of reaction product of Polyisobutylene plus Phosphorus Pentasulphide+Catalytic amount of Sulphur Powder (as per example 1) and 50% solvent.

B=Tributyl Phosphate, (as commercially available), without any solvent.

C=Di-isodecyl Phenyl Phosphite, (as commercially available), without any solvent.

The results presented in the Tables 1 to 12, show separately the effectiveness of each of the three compounds A, B, and C and also show separately the effectiveness of the each of the two mixture (A+B) and (A+C). The detailed discussion given below, shows very much improved effectiveness in high temperature naphthenic acid corrosion inhibition, of each of the two mixtures (A+B) and (A+C), as compared to effectiveness of each of the compounds. A, B and C separately. The very much improved effectiveness of the inhibiting compound of present invention, that is of either of mixtures (A+B) or (A+C) is seen from the very high corrosion inhibition efficiency, even with reduction in the total dosage of the active components.

Tables 1 to 3 show the results of effectiveness of compound A, for three different molar ratio of high Reactive Polyisobutylene to Phosphorus Pentasulphide, such as 1:1, 1:0.5 and 1:0.25. Table 4 shows results of effectiveness of compound A with molar ratio of Normal Polyisobutylene to Phosphorus Pentasulphide, such as 1:0.35.

Table 5 shows results of effectiveness of compound B that is, Tributyl Phosphate, as commercially available, without any solvent.

Table 9 shows results of effectiveness of compound C, that is Di-isodecyl Phenyl Phosphite, as commercially available, without any solvent.

Three tables 6 to 8 show effectiveness of the additive compound comprising mixture (A+B) of present invention, with two molar ratios 1:1 and 1:0.5 of two components of A, that is, High Reactive Polyisobutylene and Phosphorus Pentasulphide.

Table 10 shows effectiveness of the additive compound comprising mixture (A+C) of present invention, with molar ratio of 1:1 of High Reactive Polyisobutylene and Phosphorus Pentasulphide.

Discussion about Very High Effectiveness of Mixture (A+B), that is, Additive Compound of Present Invention, in Naphthenic Acid Corrosion Inhibition

a) Referring to Table 1, effective active dosage of compound A (molar ratio 1:1) of 300 ppm and 325 ppm were required to achieve corrosion inhibition efficiency of 95.75% and 99.67% respectively.

b) Referring to Table 2, effective active dosage of compound A (molar ratio 1:0.5) of 250 ppm was required to achieve corrosion inhibition efficiency of 75.48%.

c) Referring to Table 3, effective active dosage of compound A, (molar ratio 1:0.25) of 500 ppm and 750 ppm were required to achieve corrosion inhibition efficiency of 83.81% and 97.72% respectively.

d) Referring to Table 4, effective active dosage of compound A, with normal polyisobutylene (molar ratio 1:0.35) of 300 ppm gave corrosion inhibition efficiency of only 54.39%.

e) Referring to Table 5, effective active dosage of compound B, of 100 ppm gave corrosion inhibition efficiency of only 83:97%.

f) In contract, referring to Table 6, total effective active dosage of mixture (A+B) of 150 ppm (75 ppm of A and 75 ppm of B) and 150 ppm (90% of A and 60 ppm of B) gave corrosion inhibition efficiency of 97.49% and 99.20% respectively.

This clearly shows the inventiveness of the mixture (A+B) of present invention, as very high corrosion inhibition efficiency of about 97% and 99% are achieved with very low total effective active dosages the mixture (A+B), that is, 150 ppm. This will effect tremendous savings due to very low dosages of mixture.

Discussion about Very High Effectiveness of Mixture (A+C), that is Additive Compound of Present Invention, in Naphthenic Acid Corrosion Inhibition.

Referring to Table 9, effective active dosage of compound C, of 120 ppm and 150 ppm gave corrosion inhibition efficiency of 76.05% and 98.18%.

In contrast with results presented in Table 1 to 9, as discussed above, total effective active dosages of mixture (A+C) of present invention of 200 ppm (140 ppm of A and 60 ppm of C) gave corrosion inhibition efficiency of 99.54%. This leads to large savings, when it is noted that compound C is very expensive as compared to compound A.

Thus it is seen from the earlier discussion that the additive compounds formed by two separate mixtures, (compound A+compound B) and (compound A+compound C) of present invention used for corrosion-inhibition have the following important distinguishing feature, as compared to the prior art.

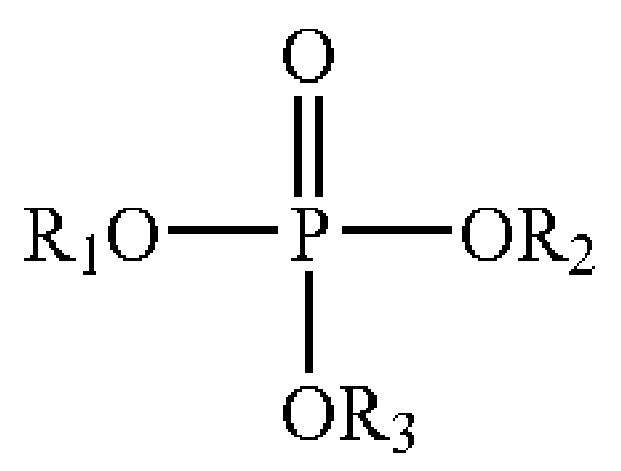
The inventor of the present invention, after extensive experimentation, has surprisingly found that the two additive combination compounds, each used by the inventor, as additive that is, two combination compounds formed by two separate mixtures, (compound A+compound B) and (compound A+compound C) are both highly effective in high temperature corrosion inhibition, as shown by the experimental results given in Tables 1 to 11.

The prior-art does not teach or suggest use of mixture (A+B) or mixture (A+C) in naphthenic acid corrosion inhibition or sulphur corrosion inhibition or any corrosion inhibition, in general.

In view of the details given in foregoing description of the present invention, it will be apparent to a person skilled in the art that the present invention basically comprises the following items:

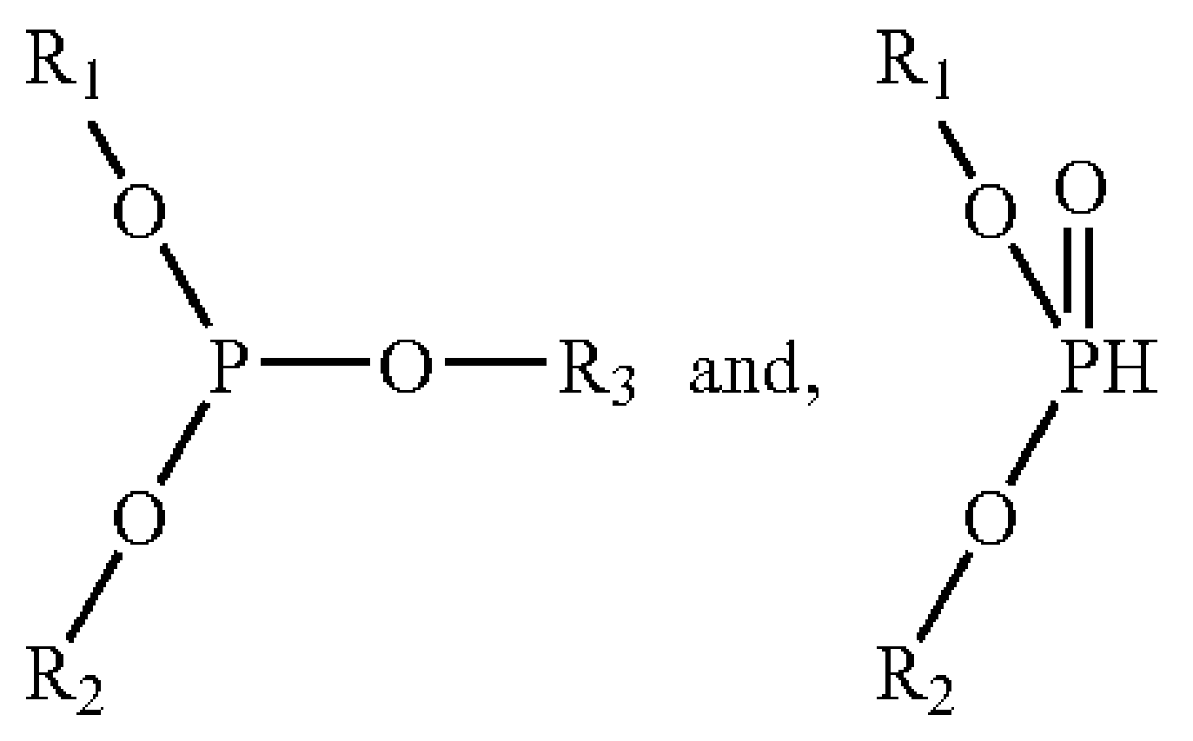
Item 1

A high temperature naphthenic acid corrosion inhibiting composition comprising a chemical mixture of corrosion inhibiting amount of an olefin Phosphorus sulphur compound A with corrosion inhibiting amount of any organophosphorus compound selected from the group consisting of compound B, compound C and compound D; wherein said olefin Phosphorus sulphur compound A, is produced by reacting said olefin with Phosphorus pentasulphide in presence of catalytic amount of sulphur, capably forming a reaction mixture, with molar ratio of said olefin to said Phosphorus pentasulphide being between 1:0.05 to 1:1.5, preferably being 1:1; wherein said compound B is a phosphate ester of the formula



$$R_1O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR_3}{|}}{P}}-OR_2$$

wherein R_1 and R_2 are each independently selected from the group consisting of hydrogen and moieties having from one to thirty carbon atoms, and R_3 is a moiety having from one to thirty carbon items; and wherein said compound C is an aryl containing phosphite compound excluding nitrogen having a structure selected from the group consisting of



wherein R_1, R_2 and R_3 are C_6 to C_{12} aryl or alkyl and at least one R group is an aryl radical; and wherein said compound D is a phosphonate.

Item 2

A composition, as described in item 1, wherein said olefin is polyisobutylene, which is either high reactive or normal.

Item 3

A composition, as described in item 1 and 2, wherein said olefin Phosphorus sulphur compound is arrived at, by stirring and heating said reaction mixture of item 1, to 160° C. under nitrogen gas purging, maintaining said reaction mixture between 160° C. to 180° C. for a period of 1 hour to 2 hours, raising temperature of said reaction mixture to from 185° C. to 250° C., preferably from 190° C. to 230° C., more preferably from 210° C. to 225° C. and maintaining said reaction mixture with raised temperature for 1 to 24 hours, preferably for 6 to 10 hours, cooling the reaction mass to 100° C. and purging nitrogen gas into reaction vessel to drive out the hydrogen sulphide gas, thereby resulting into said composition.

Item 4

A composition according to item 1, 2 or 3 wherein said olefin is an optionally substituted hydrocarbon group.

Item 5

A composition according to any one of the preceding items wherein said olefin is an optionally substituted alkyl or alkenyl group.

Item 6

A composition according to any one of the preceding items wherein said olefin is an optionally substituted branched alkyl or alkenyl group.

Item 7

A composition according to any one of the preceding items wherein said olefin has between 10 and 1000 carbon atoms.

Item 8

A composition according to any one of the preceding items wherein said olefin has between 4 and 200 carbon atoms.

Item 9

A composition according to any one of the preceding items wherein said olefin has a molecular weight of from 200 to 10,000.

Item 10

A composition according to any one of the preceding items wherein said olefin has a molecular weight of approximately 200 to approximately 1300.

Item 11

A composition, comprising said mixture of compound A and compound B of item 1 and 14, wherein said phosphate ester B is selected from group consisting of phosphate, diphosphate, triphosphate, and tributyl phosphate, preferably tributyl phosphate.

Item 12

A composition, as described in item 1, wherein said aryl containing phosphite compound C is selected from the group consisting of triphenyl phosphite, diphenyl phosphite, diphenyl isodecyl phosphite, diphenyl isooctyl phosphite, di-isodecyl phenyl phosphite and mixtures thereof, preferably di-isodecyl phenyl phosphite.

Item 13

A composition, as described in item 12, wherein said tributyl phosphate is of a type which is commercially available.

Item 14

A composition, as described in item 14, wherein said di-isodecyl phenyl phosphite is of a type which is commercially available.

Item 15

A composition, as described in items 1, 11 and 13, wherein the amount of said mixture of compound A and compound B, which should be added to crude oil for high temperature naphthenic acid corrosion inhibition, is from about 1 ppm to about 5000 ppm, preferably from about 1 ppm to about 300 ppm.

Item 16

A composition, as described in item 15, wherein the ratio of compound A to compound B, by weight, is from about 0.1:2 to about 2:0.1.

Item 17

A composition, as described in items 1, 12 and 14, wherein the amount of said mixture of compound A and compound C, which should be added to crude oil for high temperature naphthenic acid corrosion inhibition, is from about 1 ppm to about 5000 ppm, preferably from about 1 ppm to about 300 ppm.

Item 18

A composition, as described in item 17 wherein the ratio of compound A to compound C, by weight, is from about 0.1:2 to about 2:0.1.

Item 19

A composition, as described in item 1, wherein the amount of mixture of compound A and compound D, which should be added to the crude oil for high temperature naphthenic acid corrosion inhibition, is from about 1 ppm to about 5000 ppm, preferably from about 1 ppm to 300 ppm.

Item 20

A composition, as described in item 19, wherein the ratio of compound A to compound D, by weight, is from about 0.1:2 to about 2:0.1.

Item 21

A process for high temperature naphthenic acid corrosion inhibition and/or high temperature sulphur corrosion inhibition of metallic surfaces of any of the hydrocarbon, processing units, with said processing units comprising distillation columns, strippers, trays, pump around piping and related equipments, using inhibitor combination compound such as, any mixture from three mixtures, such as, a mixture of two compounds A and B of item 1, 2, 11 and 13, or a mixture of two compounds A and C of items 1, 2, 12 and 14, and a mixture of two compounds A and D of items 1, 2, 19 and 20, comprising the steps of:

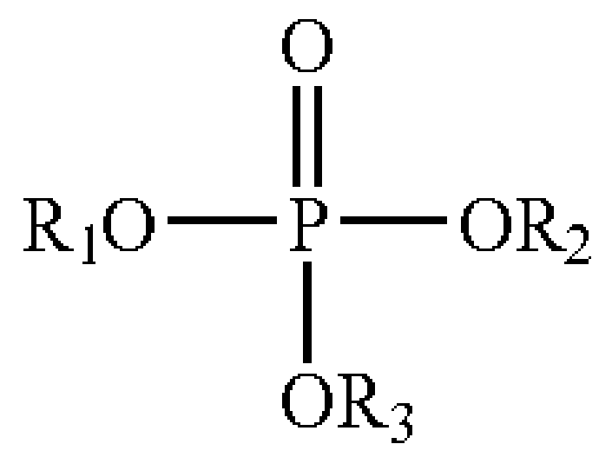
a. heating the hydrocarbon containing naphthenic acid and/or sulphur compounds, to vapourize a portion of said hydrocarbon;
b. condensing a portion of the hydrocarbon vapours, passing through said hydrocarbon processing unit, to produce a condensed distillate;
c. adding to said distillate, before said condensed distillate is returned to said hydrocarbon processing unit or collected as a product, from about 1 ppm to about 5000 ppm, preferably from about 1 ppm to 300 ppm of said inhibitor combination compound such as, any mixture from three mixtures, such as, said mixture of two compounds A and B of item 1, 2, 11 and 13, or said mixture of two compounds A and C of items 1, 2, 12 and 14, and said mixture of two compounds A and D of items 1, 2, 19 and 20, wherein ratio by weight of A to B is from about 0.1:2 to about 2:0.1 and ratio of A to C is from about 0.1:2 to about 2:0.1. and ratio by weight of A to D is from about 0.1:2 to about 2:0.1;
d. allowing said condensed distillate containing said inhibitor combination compound such as, any mixture from three mixtures, such as, said mixture of two compounds A and B of item 1, 2, 11 and 13, or said mixture of two compounds A and C of items 1, 2, 12 and 14, and said mixture of two compounds A and D of items 1, 2, 19 and 20, to contact said metallic surfaces of said hydrocarbon processing unit, to form a protective film on said surfaces whereby each surface is inhibited against corrosion; and
e. allowing said condensed distillate to return to said hydrocarbon processing unit, or to be collected as said product.

Although the invention has been described with reference to certain preferred embodiments, the invention is not meant to be limited to those preferred embodiments. Alterations to the preferred embodiments described are possible without departing from the spirit of the invention. However, the process and composition described above are intended to be illustrative only, and the novel characteristics of the invention may be incorporated in other forms without departing from the scope of the invention.

The invention claimed is:

1. A high temperature naphthenic acid corrosion inhibiting composition consisting of a chemical mixture of:

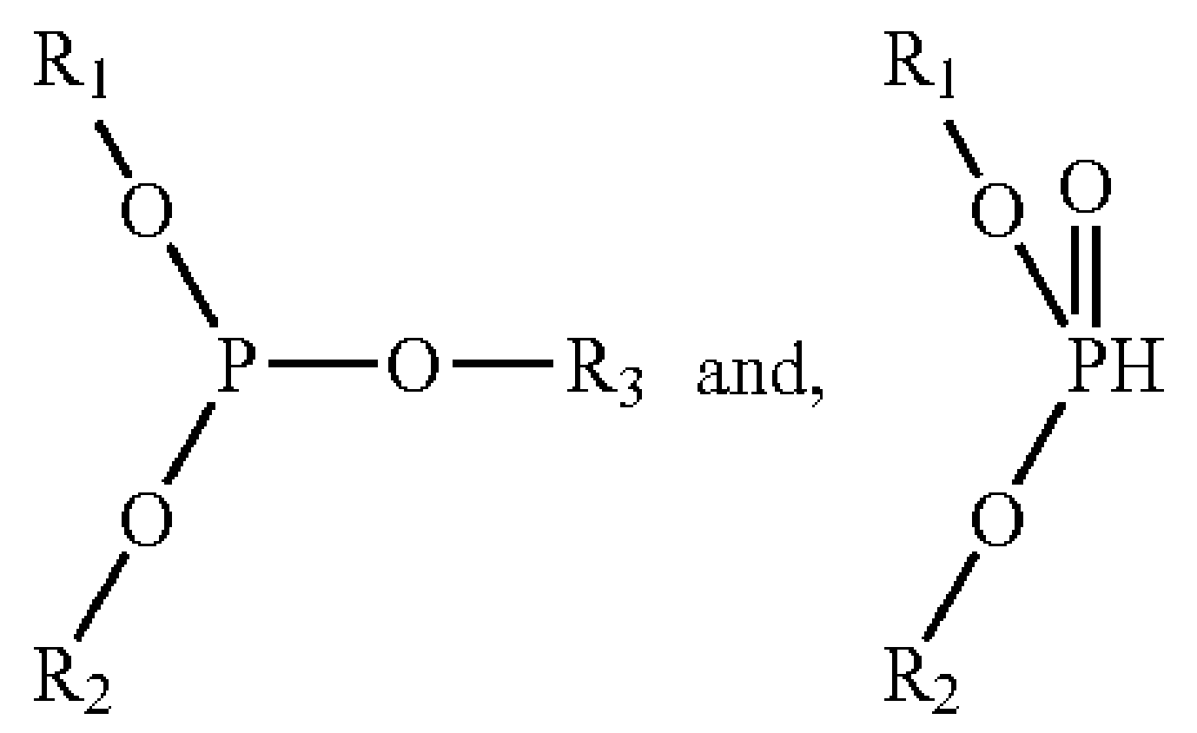
i) corrosion inhibiting amount of an olefin phosphorus sulphur compound A with
ii) corrosion inhibiting amount of any organophosphorus compound selected from the group consisting of
  a) compound B,
  b) compound C, and
  c) compound D;
  wherein said olefin phosphorus sulphur compound A is produced by reacting said olefin with phosphorus pentasulphide in presence of catalytic amount of sulphur to form a reaction mixture, with molar ratio of said olefin to said phosphorus pentasulphide being between 1:0.05 to 1:1,5;
  wherein said compound B is a phosphate ester of the formula



$$R_1O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR_3}{|}}{P}}-OR_2$$

wherein R_1 and R_2 are each independently selected from the group consisting of hydrogen and moieties having from one to thirty carbon atoms, and R_3 is a moiety having from one to thirty carbon atoms; and

wherein said compound C is an aryl containing phosphite compound excluding nitrogen having a structure selected from the group consisting of



wherein R_1 R_2 $_{and\ R3}$ are C_6 to C_{12} aryl or alkyl and at least one R group is an aryl radical; and

wherein said compound D is a phosphonate.

2. A composition, as claimed in claim **1**, wherein said olefin is polyisobutylene, which is either high reactive or normal.

3. A composition, as claimed in claim **2**, wherein said olefin phosphorus sulphur compound A is arrived at, by stirring and heating said reaction mixture of claim **1**, to 160° C. under nitrogen gas purging, maintaining said reaction mixture between 160° C. to 180° C. for a period of 1 hour to 2 hours, raising temperature of said reaction mixture to from 185° C. to 250° C. and maintaining said reaction mixture with raised temperature for 1 to 24 hours, cooling the reaction mass to 100° C. and purging nitrogen gas into reaction vessel to drive out the hydrogen sulphide gas, thereby resulting into said compound A.

4. A composition according to claim **1**, wherein said olefin has between 10 and 1000 carbon atoms.

5. A composition according to claim **1**, wherein said olefin has between 4 and 200 carbon atoms.

6. A composition according to claim **1**, wherein said olefin has a molecular weight of from 200 to 10,000.

7. A composition according to claim **6**, wherein said olefin has a molecular weight of approximately 200 to approximately 1300.

8. A composition, consisting of said mixture of compound A and compound B of claim **1**, wherein said phosphate ester B is selected from group consisting of phosphate, diphosphate, triphosphate, and tributyl phosphate.

9. A composition, as claimed in claim **1**, wherein said aryl containing phosphite compound C is selected from the group consisting of triphenyl phosphite, diphenyl phosphite, diphenyl isodecyl phosphite, diphenyl isooctyl phosphite, di—isodecyl phenyl phosphite and mixtures thereof.

10. A composition, as claimed in claim **1**, further comprising tributyl phosphate, wherein tributyl phosphate is of a type which is commercially available.

11. A composition, as claimed in claim **9**, wherein said di—isodecyl phenyl phosphite is of a type which is commercially available.

12. A composition, as claimed in claim **1**, wherein the amount of said mixture of compound A and compound B, which should be added to crude oil for high temperature naphthenic acid corrosion inhibition, is from about 1 ppm to about 5000 ppm.

13. A composition, as claimed in claim **12**, wherein the ratio of compound A to compound B, by weight, is from about 0.1:2 to about 2:0.1.

14. A composition, as claimed in claim **1**, wherein the amount of said mixture of compound A and compound C, which should be added to crude oil for high temperature naphthenic acid corrosion inhibition, is from about 1 ppm to about 5000 ppm.

15. A composition, as claimed in claim **14**, wherein the ratio of compound A to compound C, by weight, is from about 0.1:2 to about 2:0.1.

16. A composition, as claimed in claim **1**, wherein the amount of mixture of compound A and compound D, which should be added to the crude oil for high temperature naphthenic acid corrosion inhibition, is from about 1 ppm to about 5000 ppm.

17. A composition, as claimed in claim **16**, wherein the ratio of compound A to compound D, by weight, is from about 0.1:2 to about 2:0.1.

18. A process for high temperature naphthenic acid corrosion inhibition of metallic surfaces of any of the hydrocarbon processing units comprising distillation columns, strippers, trays, pump around piping and related equipments, using high temperature naphthenic acid corrosion inhibiting composition consisting of a chemical mixture of corrosion inhibiting amount of an olefin phosphorus sulphur compound A with corrosion inhibiting amount of any organophosphorus compound selected from the group consisting of compound B, compound C and compound D as claimed in claim **1**, comprising the steps of:

a. heating the hydrocarbon containing naphthenic acid compounds, to vapourize portion of said hydrocarbon;

b. condensing a portion of the hydrocarbon vapours, passing through said hydrocarbon processing unit, to produce a condensed distillate;

c. adding to said distillate, before said condensed distillate is returned to said hydrocarbon processing unit or collected as a product, from about 1 ppm to about 5000 ppm of said high temperature naphthenic acid corrosion inhibiting composition, wherein ratio by weight of said compound A to said compound B is from about 0.1:2 to about 2:0.1 and ratio of said compound A to said compound C is from about 0.1:2 to about 2:0.1, and ratio by weight of said compound A to said compound D is from about 0.1:2 to about 2:0.1;

d. allowing said condensed distillate containing said high temperature naphthenic acid corrosion inhibiting composition to contact said metallic surfaces of said hydrocarbon processing unit, to form a protective film on said surfaces whereby each surface is inhibited against corrosion; and

e. allowing said condensed distillate to return to said hydrocarbon processing unit, or to be collected as said product.

19. A process as claimed in claim **18**, wherein said olefin is polyisobutylene, which is either high reactive or normal.

20. A process according to claim **18**, wherein said olefin is an optionally substituted hydrocarbon group.

21. A process according to claim **18**, wherein said olefin has between 4 and 1000 carbon atoms.

22. A process according to claim **18**, wherein said olefin has a molecular weight of from 200 to 10,000.

23. A process as claimed in claim **18**, wherein said phosphate ester B is selected from group consisting of phosphate, diphosphate, triphosphate, and tributyl phosphate.

24. A process as claimed in claim **18**, wherein said high temperature naphthenic acid corrosion inhibiting composition further comprises tributyl phosphate wherein said tributyl phosphate is of a type which is commercially available.

25. A process as claimed in claim **18**, wherein said aryl containing phosphite compound C is selected from the group consisting of triphenyl phosphite, diphenyl phosphite, diphenyl isodecyl phosphite, diphenyl isooctyl phosphite, di—isodecyl phenyl phosphite and mixtures thereof.

26. A process as claimed in claim **25**, wherein said di—isodecyl phenyl phosphite is of a type which is commercially available.

27. A process as claimed in claim **18**, wherein said hydrocarbon containing naphthenic acid compound also contains sulphur compounds.

28. A composition, as claimed in claim **1**, wherein said molar ratio of said olefin to said phosphorus pentasulphide is 1:1.

29. A composition, as claimed in claim **3**, wherein said raising temperature of said reaction mixture varies from 190° C. to 230° C.

30. The composition as claimed in claim **3**, wherein said raising temperature of said reaction mixture varies from 210° C. to 225° C.

31. The composition as claimed in claim **3**, wherein said reaction mixture with raised temperature is maintained for 6 to 10 hours.

32. A composition, as claimed in claim **12**, wherein the amount of said mixture of compound A and compound B, which should be added to crude oil for naphthenic acid corrosion inhibition varies from about 1 ppm to about 300 ppm.

33. A composition, as claimed in claim **14**, wherein the amount of said mixture of compound A and compound C, which should be added to crude oil for naphthenic acid corrosion inhibition varies from about 1 ppm to about 300 ppm.

34. A composition, as claimed in claim **16**, wherein the amount of mixture of compound A and compound D, which should be added to the crude oil for naphthenic acid corrosion inhibition varies from about 1 ppm to 300 ppm.

35. A composition, as claimed in claim **1**, wherein polyisobutylene is polyisobutylene containing greater than 70% of vinyledene double bond.

36. A composition, as claimed in claim **1**, wherein polyisobutylene is polyisobutylenes containing vinyl, vinyledene.

37. A process as claimed in claim **18**, wherein about 1 ppm to 300 ppm of said inhibitor composition is added to said distillate.

38. A method of using naphthenic acid corrosion inhibiting composition of claim **1** for naphthenic acid corrosion inhibition of metallic surfaces of the hydrocarbon processing units comprising distillation columns, strippers, trays, pump around piping and related equipments, wherein the composition consists of a chemical mixture of (i) an olefin phosphorus sulphur compound A and (ii) an organophosphorus compound selected from the group consisting of compound B, compound C and compound D of claim **1**, and wherein the method comprises the steps of:

a. heating the hydrocarbon containing naphthenic acid compounds to vapourize a portion of said hydrocarbon;

b. condensing a portion of the hydrocarbon vapours, passing through said hydrocarbon processing unit, to produce a condensed distillate;

c. adding to said distillate, before said condensed distillate is returned to said hydrocarbon processing unit or collected as a product, said naphthenic acid corrosion inhibiting composition,

d. allowing said condensed distillate containing said naphthenic acid corrosion inhibiting composition to contact said metallic surfaces of said hydrocarbon processing unit, to form a protective film on said surfaces whereby each surface is inhibited against corrosion; and

e. allowing said condensed distillate to return to said hydrocarbon processing unit, or to be collected as said product.

39. The method as claimed in claim **38**, wherein from about 1 ppm to about 5000 ppm of said composition is added in step c.

40. The method as claimed in claim **38**, wherein ratio by weight of said compound A (component (i) of the composition) to said compound B, C or D (component (ii) of the composition) varies from about 0.1:2 to about 2:0.1.

41. The method as claimed in claim **38**, wherein said olefin is polyisobutylene, which is either high reactive or normal.

42. The method as claimed in claim **41**, wherein said olefin has between 4 and 1000 carbon atoms.

43. The method as claimed in claim **41**, wherein said olefin has a molecular weight of from 200 to 10,000.

44. The method as claimed in claim **38**, wherein said organophosphorus compound B is selected from group consisting of phosphate, diphosphate, triphosphate, and tributyl phosphate.

45. The method as claimed in claim **38**, wherein said naphthenic acid corrosion inhibiting composition further comprises tributyl phosphate.

46. The method as claimed in claim **38**, wherein said organophosphorus compound C is selected from the group consisting of triphenyl phosphite, diphenyl phosphite, diphenyl isodecyl phosphite, diphenyl isooctyl phosphite, di-isodecyl phenyl phosphite and mixtures thereof.

47. The method as claimed in claim **38**, wherein said hydrocarbon containing naphthenic acid compound also contains sulphur compound.

48. The method as claimed in claim **39**, wherein about 1 ppm to 300 ppm of said inhibitor composition is added to said distillate.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 9,228,142 B2
APPLICATION NO. : 12/594320
DATED : January 5, 2016
INVENTOR(S) : Mahesh Subramaniyam

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Claims

Claim 1, col. 24, line 43, replace "$R_{2\ and\ R3}$" with --R_2 and R_3--

Signed and Sealed this
Nineteenth Day of April, 2016

Michelle K. Lee

Michelle K. Lee
Director of the United States Patent and Trademark Office